THERMAL DIFFUSION IN THE CRITICAL REGION

BY

NORWIN CALEY PIERCE

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AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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THERMAL DIFFUSION IN THE CRITICAL REGION

Introduction

Thermal diffusion is the transport of molecules of a mixture caused by a temperature gradient. In the absence of convection currents, the steady state concentration gradient of the mixture is such that the rate of separation caused by thermal diffusion is balanced by the remixing of ordinary diffusion.

Thermal diffusion was theoretically predicted by Enskog (5) in 1911 and independently by Chapman (2) in 1917. In 1939 Chapman and Cowling (3) published a comprehensive treatise of the theory of non-uniform gases expressing the gas coefficients as general functions of the laws of molecular interaction. Hirshfelder et al. (8) have evaluated the general functions for the Lennard-Jones model, a relatively realistic law of molecular interaction.

The thermal diffusion column first developed by Clusius and Dickel (4) and later refined by Brewer and Bramley (1) utilized the effect of vertical convection to magnify the separation caused by thermal diffusion to such an extent that the columns were useful for isotope separation.

The thermal diffusion coefficient is peculiar among the gas coefficients in that its value is extremely sensitive to the interaction potential existing between the molecules. The law of interaction may be best determined by thermal diffusion measurements.

The purpose of this experiment is to investigate the molecular interaction in the critical region by measurement of thermal diffusion for a xenon-ethane mixture (0.18 mole percent xenon). It has been postulated that clusters of molecules form in the gas at temperatures near saturation (9, 10). For a finite temperature range above the normally defined critical temperature and near the critical volume, the

size of these clusters becomes large, and their equilibrium size distribution is a function of the thermal history of the system. The formation of such clusters should affect the thermal diffusion coefficient which is most sensitive to the molecular interaction.

Theory

For the Lennard-Jones model, the thermal diffusion ratio (the ratio of the thermal diffusion coefficient to the ordinary diffusion coefficient divided by the mole fractions of both components) is a function of temperature but is independent of pressure. Enskog's dense gas theory (6) predicts that the thermal diffusion ratio will increase with increasing pressure becoming 25 percent higher at the critical point than for a dilute gas for the xenon-ethane system. The dense gas theory is based on the assumption of molecular chaos and employs the rigid elastic spherical model. Molecular chaos cannot be assumed for a system in which clusters form, and the mathematically convenient elastic spherical model is not realistic. Molecular chaos was also assumed by Chapman and Enskog in the derivation of the gas coefficients for a dilute gas.

The hydrodynamical equations for the thermal diffusion column have been developed by Furry et al. (7). The relationship between the column separation obtained, q, and the thermal diffusion ratio, α, is given by

$$q \equiv \ln\left[\left(\frac{X_1}{X_2}\right)_{\text{Bottom}}\left(\frac{X_2}{X_1}\right)_{\text{Top}}\right] = \frac{63\,\Gamma\,L\,\alpha}{2Tw^4g}\left[\frac{1}{1+5670\left(\frac{\Gamma}{2gw^4\left(\frac{dT}{dx}\right)}\right)^2}\right]$$

where X_1, X_2 = mole fractions of xenon, ethane
L = column length, cm.
w = effective column annular gap, cm.
$\frac{dT}{dx}$ = temperature gradient across column gap, °C/cm.
$\Gamma = \eta D/\beta$

η = viscosity of fluid, poises
D = diffusion coefficient, sq. cm./ sec.
β = negative temperature coefficient of density, gm./cu. cm. °C
g = acceleration of gravity

Experimental Apparatus And Procedure

The thermal diffusion column consists of two concentric steel tubes mounted vertically. The inner tube of the column was ground to 0.7600 inches (+0.0002″, −0.0000″) outside diameter, and the outer tube honed to 0.8000 inches (+0.0005″, −0.0000″) inside diameter. The tubes were spaced to give an annular gas column of 0.0508 cm. in width and 41.6 cm. long. Accurate tube spacing was maintained by inserting 0.020″ piano wire spacers at each end of the column. Sampling chambers and sampling valves were provided at each end of the column, and a gas inlet connection was installed in the center of the column.

Outer and inner tube temperatures were maintained by circulating water from two constant temperature baths through the outer tube jacket and inner tube. Column pressure was measured by balancing the gas pressure with oil through a mercury U-tube. Three calibrated gages of range 0 — 1500, 0 — 200, and 500 — 800 psi. were connected to the oil line.

The xenon-ethane gas mixture was stored in a cylinder at a pressure higher than the column operating pressure. The inner and outer tubes were brought to the desired temperatures and the gas admitted until the desired pressure was reached. The column was allowed to operate for a length of time equal to at least four relaxation times as defined by Furry. Samples were taken from each end of the column and analyzed by counting the radioactive Xe^{133} tracer with a Geiger counter. The probable counting error was less than 0.1 percent for runs in the critical region and increased to 0.22 percent for the low pressure runs.

The ethane was purchased from the Phillips Petroleum Company and was designated as 99.9 percent pure, the most probable impurity being propane. The xenon was purchased from the Matheson Company and irradiated in an atomic pile at the Argonne National Laboratories. The xenon was spectroscopically pure. The critical temperature of the mixture is 32.28°C, critical pressure, 48.7 atm., and critical density, 0.2122 gm./cc.

Experimental Results

The thermal diffusion ratio for the system xenon-ethane is presented in Table 1. The value of α is calculated by Equation 1 where the effective column gap is 0.96 times the measured (0.0508 cm.) gap. A positive value of the thermal diffusion ratio indicates a greater concentration of ethane at the top of the column. The temperature reported is the linear average of the hot and cold tube temperatures.

The thermal diffusion ratio decreases rapidly as the critical density is approached in sharp contrast to the behavior predicted by the Lennard-Jones model corrected by the dense gas theory. As the density decreases, the value of the thermal diffusion ratio approaches that predicted by the Lennard-Jones model for a dilute gas. Above a relatively low density (about 0.005 for $t = 50°C$, $P = 4.5$ atm.) the value of the thermal diffusion ratio becomes negative indicating that ethane is acting "heavier" than xenon. In order to satisfy the theoretical equations for α using the Lennard-Jones model, the apparent weight of ethane must increase to the order of 10^5 times the mass of a xenon molecule at densities near the critical. At gas densities of one-half the critical density the effective weight of the ethane clusters is 10^3 that of a xenon molecule.

At higher densities the thermal diffusion ratio becomes positive for both dense gas and liquid, agreeing, at least in order of magnitude, to that predicted by theory for a dilute gas indicating that the ethane clusters do not affect the trans-

port of molecules.

Since a finite temperature difference was required for experimental control, it was not possible to reduce the average temperature to the critical temperature. However, it is not unreasonable to expect that the thermal diffusion ratio should be reduced to an even larger negative value at temperatures closer to the critical and at the critical density.

TABLE 1

THE THERMAL DIFFUSION RATIO FOR XENON-ETHANE

Temperature °C	Pressure Atm.	Density gm./cc.	α
58.7	4.14	0.004686	+ 0.0291
58.9	4.82	0.005487	+ 0.0078
58.6	7.37	0.008555	— 0.0037
57.7	7.88	0.009268	— 0.0024
49.8	4.60	0.005393	— 0.0090
49.7	4.67	0.005476	+ 0.0025
34.0	5.01	0.006226	— 0.0370
38.7	7.69	0.009570	— 0.0249
38.3	26.2	0.03852	— 0.0482
33.9	32.6	0.05386	— 0.1279
31.6	38.9	0.0748	— 0.392
31.6	39.9	0.0783	— 0.496
42.0	46.6	0.0919	— 0.571
42.3	46.7	0.0921	— 0.620
42.6	49.2	0.1026	— 0.939
43.0	49.7	0.1043	— 0.980
43.2	51.6	0.1150	— 1.30
43.2	51.8	0.1160	— 1.27
39.2	46.0	0.0942	— 0.698
39.2	46.1	0.0945	— 0.705
39.2	49.6	0.1147	— 1.628
39.0	49.6	0.1153	— 1.807
39.0	52.0	0.1376	— 2.74
38.8	52.0	0.1394	— 2.91

Temperature °C	Pressure Atm.	Density gm./cc.	a
35.7	46.7	0.1058	— 1.304
35.9	46.9	0.1070	— 1.371
35.9	49.1	0.1264	— 2.93
36.0	49.7	0.1329	— 3.85
35.9	51.6	0.1855	— 12.33
35.9	51.6	0.1855	— 13.00
33.8	46.6	0.1128	— 2.02
33.6	46.9	0.1161	— 2.41
33.85	49.7	0.1781	— 22.9
33.8	49.6	0.1790	— 41.0
33.8	49.7	0.1850	— 18.9
33.7	49.8	0.2019	— 23.4
33.8	51.2	0.2560	— 5.34
33.8	51.2	0.2560	— 5.23
32.4	49.6	0.2757	— 5.53
33.6	58.4	0.3163	+ 0.183
		Liquid Runs	
32.0	49.6	0.2764	— 2.78
30.5	49.5	0.3072	— 0.224
30.5	49.5	0.3077	0.00
28.4	48.4	0.3193	+ 0.628
28.4	48.9	0.3240	+ 0.717
25.0	46.3	0.3373	+ 1.094
25.0	47.1	0.3390	— 0.048
20.4	42.1	0.3545	+ 0.902
20.4	43.5	0.3560	+ 0.875

Conclusions

1. The assumption of molecular chaos is not applicable to a xenon-ethane gas mixture near the critical region due to the formation of ethane "clusters". The general expressions involving the distribution function cannot be expected to apply to a system in which clusters form. The value of a predicted by the dense gas theory is not of the correct order of magnitude

in this region.

2. The mass of the ethane clusters formed near the critical density at temperatures just above the critical temperature is of the order of 10^5 times the mass of a xenon molecule.

3. The effect of ethane cluster formation is apparent at pressures as low as 4.14 atmospheres.

4. There is little tendency for ethane to form selective clusters which affect the thermal diffusion ratio in the liquid and dense gas regions.

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VITA

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